Vanadium(V) Oxoperoxo Complexes with Side Chain Substituted *N*-Salicylidenehydrazides: Modeling Supramolecular Interactions in Vanadium Haloperoxidases

Simona Nica,[a] Axel Pohlmann,[a] and Winfried Plass*[a]

Dedicated to Professor Dirk Walther on the occasion of his 65th birthday

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The Schiff-base ligand derived from salicylaldehyde and γ-hydroxybutanoic acid hydrazide (H_2Salhyhb) reacts with potassium metavanadate and hydrogen peroxide in a water/methanol solution with a pH value of around two to yield the corresponding vanadium(V) oxoperoxo complex [VO(O_2)-HSalhyhb(H_2O)] (**1**). Complex **1** crystallizes with one molecule of water as **1**·H_2O in the monoclinic space group $P2_1/n$. For the vanadium atom a pentagonal-bipyramidal coordination geometry is observed, with a side-on bonded peroxo ligand in the equatorial plane. The hydroxy side chain of the hydrazide ligand is involved in a hydrogen-bond network with the peroxo ligand at the vanadium atom. This network shows some similarities with the hydrogen-bonding scheme found for the peroxo form of vanadium haloperoxidases. The stoichiometric reaction of **1** with 1,3,5-trimethoxybenzene (TMB) in the presence of tetrabutylammonium bromide leads to the formation of 1-bromo-2,4,6-trimethoxybenzene (Br-TMB), thus mimicking the oxidative halogenation function of the native enzyme. Complex **1** is also capable of oxidizing triphenylphosphane and methylphenylsulfane, yielding a *cis*-dioxovanadium(V) complex and the corresponding phosphane or sulfane oxide, respectively.

Introduction

Vanadium haloperoxidases (VHPO) are enzymes capable of catalyzing halide oxidation by hydrogen peroxide to give the corresponding hypohalous acid.[1] This oxidized intermediate can halogenate various organic substrates,[2] or react with a second equivalent of hydrogen peroxide to produce singlet oxygen.[3] Moreover, these enzymes can also catalyze the oxidation of organic sulfanes to sulfane oxides.[4] The active site of this class of enzyme consists of a vanadate moiety with proposed trigonal bipyramidal geometry covalently bonded to a histidine residue and held within the protein by strong hydrogen-bonding interactions with several amino acid residues.[5] This active site architecture is also found in certain acid phosphatases,[6] but subtle differences concerning the relative positions of the amino acid residues are apparent,[7] in particular, for those residues that can potentially hydrogen bond with the equatorial oxygen atoms of the vanadate moiety (i.e. lysine, arginine, and serine). Recent theoretical studies and spectroscopic data for vanadium haloperoxidases suggest that the prosthetic group is a doubly protonated $[VO_2(OH)_2]^-$ vanadate moiety.[8]

Spectroscopic and kinetic studies of the native enzyme showed that no change occurs in the redox state of the prosthetic during the catalytic cycle.[9] Thus, it was proposed that the vanadate functions as a Lewis acid catalyst, reacting with hydrogen peroxide first to form a side-on bonded peroxo ligand, which in turn may be activated through hydrogen-bonding interactions with the first shell of amino acids and nearby water molecules.[10] This is proposed to activate the peroxo intermediate by protonation which would increase the electrophilicity of the oxygen atoms of the peroxo group, thus making attack by a halide ion more favorable.[11] This mechanistic feature is also found for the heterolytic cleavage of O–O bonds in heme-based peroxidase enzymes.[12] On the basis of this aspect of the biological function of vanadate in VHPO, the synthesis of structural models with relevant hydrogen-bonding interactions has recently been reported.[13–18]

Renirie et al. spectrophotometrically determined the stability and reactivity of such a peroxo intermediate.[19] The peroxo complex is very stable at a pH value of 8 and exists for a long period of time, but is less stable at a pH value of 5 (the pH for optimum activity for the native enzyme). However, under both conditions, the enzyme is capable of oxidizing chloride ions to hypochloric acid by a pseudo first

[a] Institut für Anorganische und Analytische Chemie,
Friedrich-Schiller-Universität Jena,
Carl-Zeiss-Promenade 10, 07745 Jena, Germany
Fax: +49-3641-948132
E-mail: Sekr.Plass@uni-jena.de

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order reaction. Moreover, mutagenesis studies of vanadium chloroperoxidase proved that the amino acid residues His404, Arg490, Arg360, and Ser402 perform an essential role in haloperoxidase-catalyzed reactions.[20] All of these residues are involved in hydrogen-bonding interactions with the prosthetic group. The proposed bromination of the serine residue during the catalytic turnover has become a matter of debate in recent years.[21] This crucial role could neither be confirmed by site-directed mutagenesis studies,[22] nor by catalytic studies of model systems containing a relevant hydroxy side chain.[17] However, in mutagenesis studies a significant decrease in the enzyme activity could be observed for the chlorination and bromination reactions to about 4 and 20%, respectively.[22] This indicates that the serine residue, although not crucial, plays an important role in affecting the reactivity of the active site.

We recently reported on vanadium(v) complexes derived from the *N*-salicylidene-hydrazide ligand system that exhibit extensive hydrogen bonding.[13–17] Herein we report on the structure and reactivity of the first vanadium(v) oxoperoxo complex with a hydroxy substituted side chain, a basic ligand system that participates in hydrogen-bonding interactions relevant for vanadium haloperoxidases.

Results and Discussion

The new Schiff base ligand derived from 4-hydroxybutanoic acid hydrazide and salicylaldehyde (H_2Salhyhb) reacts with potassium vanadate and hydrogen peroxide in a methanol/water solution at 0 °C in the presence of perchloric acid to afford the orange vanadium(v) oxoperoxo complex [VO(O_2)HSalhyhb·H_2O] (**1**). Due to the acidic reaction conditions the tridentate carbonic acid hydrazide ligand is present in the mono anionic form, and upon coordination it yields the neutral complex **1**. It is worth noting that for vanadium(v) complexes with this kind of ligand system, it has been shown that the N–H proton of the amide group can be reversibly removed, leading to a variable protonation state for this ligand.[14,15,17] Complex **1** dissolves in various organic solvents like alcohols, acetonitrile, and DMF, without undergoing decomposition. The ^{51}V NMR spectrum of **1** recorded in CD_3OD reveals a single resonance in the typical range, i.e. at –551 ppm with a peak width at half height of $\Delta\nu_{1/2}$ = 105 Hz. In [D_6]DMSO complex **1** undergoes fast decomposition as indicated by the appearance of two resonance peaks in the ^{51}V NMR spectrum. The peak at –539 ppm ($\Delta\nu_{1/2}$ = 860 Hz) is attributed to the *cis*-dioxocomplex and the second peak at –572 ppm ($\Delta\nu_{1/2}$ = 1100 Hz) is assigned to the corresponding dimeric *cis*-dioxocomplex; the intensity ratio for the two peaks is approximately 10:1. Both resonances are present immediately after the dissolution of compound **1** in [D_6]DMSO. The molecular structure of complex **1**, as determined by X-ray crystallography, reveals a pentagonal-bipyramidal geometry for the coordination around the vanadium atom, as depicted in Figure 1. The hydrazide ligand coordinates in the mono anionic form, providing an ONO donor set. In the equatorial plane, the vanadium atom is coordinated to atoms O2 and O3 of the side-on bonded peroxo group, and to the donor atoms O4, O5, and N1 of the tridentate hydrazide ligand. The axial positions of the coordination polyhedra are occupied by the oxo group O1 and by the oxygen atom O7 of the coordinated water molecule. The structural parameters given in Figure 1 are consistent with those observed for other vanadium(v) complexes containing hydrazide ligands,[14,15,17,23] and with those reported for vanadium(v) oxoperoxo complexes which generally feature the vanadium atom coordinated to the oxo group in the axial position and the peroxide bound in the equatorial position.[11,18,24] Complex **1** crystallizes with one molecule of water (O8) leading to an extensive hydrogen-bond network in the solid state, as depicted in Figure 2. The first sphere of hydrogen-bonding interactions shown in Figure 2 is located below the plane of the ligand arrangement in a *trans* orientation with respect to the oxo group O1. Consequently, the oxo group O1 and the carbonyl group O5 of the hydrazide ligand are not involved in the hydrogen-bond network, which is in agreement with their relatively low donor ability. Both enantiomers are present in the crystal structure of **1**·H_2O and form hydrogen-bonded chains through the interaction between the protonated hydrazide nitrogen atom, N2, and the peroxo group of a neighboring complex of same enantiomeric form (N2···O2A 280, N2···O3A 305 pm). These two enantiomeric chains form a bilayer that incorporates the hydrogen-bond network shown in Figure 2, and in turn leads to one-dimensional hydrogen-bonded chains parallel to [010] (see Figure 3).

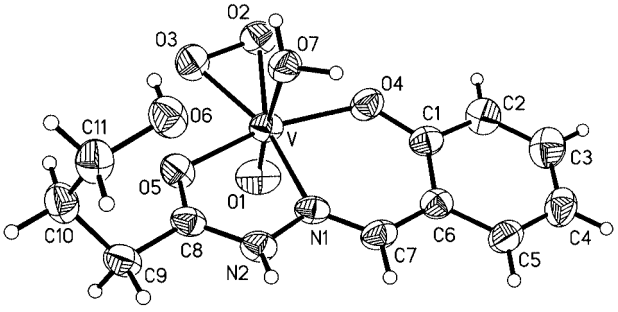

Figure 1. Molecular structure and numbering scheme for **1**. Thermal displacement ellipsoids are drawn at the 50% probability level. Selected bonds lengths [pm] and angles [°]: V–O1 157.8(3), V–O2 189.1(3), V–O3 187.6(3), V–O4 197.6(3), V–O5 207.6(3), V–O7 225.8(3), V–N1 213.2(3), O2–O3 142.9(4); O1–V–O2 103.48(13), O1–V–O3 101.94(14), O1–V–O4 97.52(15), O1–V–O5 94.26(14), O1–V–O7 170.08(13), O2–V–O3 44.57(12), O2–V–O4 79.39(12), O2–V–O5 119.93(12), O2–V–O7 86.31(12), O3–V–O4 123.41(13), O3–V–O5 75.86(12), O3–V–O7 86.08(12), O4–V–O5 154.21(12), O4–V–O7 82.58(11), O5–V–O7 81.95(11), O1–V–N1 94.16(13), O2–V–N1 155.91(12), O3–V–N1 146.81(13), O4–V–N1 82.17(12), O5–V–N1 74.14(12), O7–V–N1 76.01(11).

A situation reminiscent of the role of the active site lysine residue in VHPO[10] is found by considering the hydrogen-bond interaction between the peroxo ligand (O2 and O3) and the acidic N–H group of the hydrazide ligand (N2).[14,15,17] A second type of hydrogen-bond pathway related to the peroxo group originates from the hydroxy side

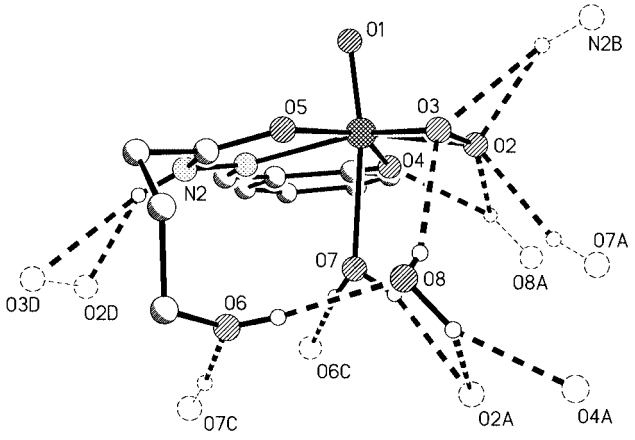

Figure 2. Hydrogen-bond network for complex **1**·H_2O. Only hydrogen atoms bonded to non-carbon atoms are shown, broken lines represent hydrogen bonds, dashed circles and lines represent symmetry equivalent atoms and the bonds between them, respectively (symmetry operators A: 1 – *x*, –*y*, –*z*; B: *x*, *y* – 1, *z*; C: 1 – *x*, 1 – *y*, –*z*; D: *x*, 1 + *y*, *z*). Selected hydrogen bond lengths [pm]: N2···O2D 280.2, N2···O3D 305.2, O6···O8 286.0, O7···O2A 282.7, O7···O6C 271.1, O8···O2A 306.0, O8···O3 299.8, O8···O4A 295.8.

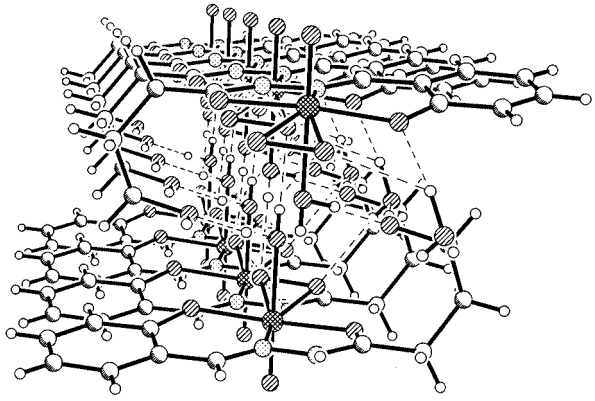

Figure 3. Representation of the hydrogen-bonded bilayer for complex **1**·H_2O, as viewed approximately along the [010] direction.

chain (O6) of the hydrazide ligand system. This side chain is involved in a hydrogen-bonding cascade that includes the water oxygen atom O8 (O6···O8 286 pm); this then leads to an intramolecular interaction with the oxygen atom O3 of the peroxo group (O8···O3 299 pm), and an intermolecular interaction with the peroxo oxygen atom O2 (O8···O2A 306 pm) of a neighboring complex. The latter of these hydrogen bonds is part of a bifurcated interaction between O8 and atoms O2 and O4 (see Figure 2). The hydrogen-bond network is completed by the oxygen atom of the coordinated water molecule, O7, which forms intermolecular contacts with the hydroxy side chain oxygen atom O6 (O6C···O7 271 pm) and with the peroxo oxygen atom O2 (O7···O2A 283 pm) of two different neighboring molecules from opposite enantiomeric chains. The observed hydrogen-bonding interactions are of specific interest due to the presence of the Ser402 residue in the active site of VHPO, in particular, they are of possible relevance to proton transfer reactions.[8]

For VHPO enzymes, a peroxo species has been proposed as an intermediate in the catalytic cycle.[10] Moreover, *cis*-dioxovanadium(V) complexes have been reported as structural and functional models for vanadium haloperoxidases that are capable of catalyzing bromination reactions with hydrogen peroxide in DMF.[25] To probe the haloperoxidase activity of complex **1**, we investigated its ability to catalyze the formation of an oxidizing bromine species. We monitored the formation of the bromo derivatives of 1,3,5-trimethoxybenzene (TMB). TMB is strongly activated towards electrophilic substitution, and can act as a quenching agent. Complex **1** reacts with one equivalent of TMB, in the presence of excess tetra-*n*-butylammonium bromide, and one equivalent of perchloric acid to yield Br-TMB. About 90% of TMB was converted to the corresponding brominated compound in less than 30 min (as monitored by HPLC). It should be noted that in the absence of acid no brominated products could be observed.

Another important reaction catalyzed by VHPO is the oxidation of organic sulfanes to sulfane oxides.[4] Although the mechanism for this reaction is not yet known, it is thought to proceed via a peroxo intermediate. To probe the sulfoxidation reactivity of the reported vanadium(V) oxoperoxo complex, **1** was treated with one equivalent of methylphenylsulfane in a methanol/dichloromethane mixture as solvent. The methylphenylsulfane was oxidized slowly, and about 75% conversion to the corresponding sulfane oxide occurred in about 48 h. It is interesting to note that this is about the same length of time usually observed for a comparable rate of conversion in model systems in which only 1 mol-% of the vanadium catalyst is present.[26] The oxidative capacity of **1** was further tested by investigating its reaction with triphenylphosphane in acetonitrile solution. This reaction was monitored by ^{31}P NMR spectroscopy – the phosphane oxide is readily formed together with the corresponding *cis*-dioxovanadium(V) complex, implying that full conversion of the reactants had occurred.

Conclusions

In this contribution the first example of a vanadium(V) oxoperoxo complex with a hydroxy side chain substituted ligand system is reported. This complex is of interest due to the presence of a serine residue within the active site environment of the prosthetic group. The importance of this residue is exemplified by the vast number of hydrogen-bonding interactions observed, which are involved in pathways relevant to the enzymatic activity. The complex is capable of generating hypobromic acid, which in turn can brominate 1,3,5-trimethoxybenzene as the organic substrate, thus modeling the corresponding enzyme reaction. Moreover, the oxidation of methylphenylsulfane and triphenylphosphane can be preformed by the reported vanadium(V) oxoperoxo complex.

Experimental Section

General Remarks: *N*,*N*-Dimethylformamide was purified and distilled prior to use. All other chemicals and solvents were of analyti-

cal reagent grade and were used as received. The reaction with triphenylphosphane was carried out under argon using standard Schlenk techniques. Perchloric acid was standardized by potentiometric titration with 1 M NaOH solution utilizing a Mettler Toledo DL 50 titrator. ^{1}H, ^{13}C, and ^{51}V NMR spectra were recorded with Bruker AVANCE 200 and 400 MHz spectrometers. The chemical shift values for ^{51}V are reported relative to $VOCl_3$ as external standard. All NMR spectra were recorded at room temperature. Elemental analyses (C, H, N) were carried out with a Leco CHNS-932 elemental analyzer. Mass spectra were measured with a MAT95XL Finnigan instrument utilizing electron spray ionization and observations were made in the negative mode. IR spectra were recorded with a Bruker IFS55/Equinox spectrometer on samples prepared as KBr pellets. Gas chromatography measurements were performed with a SRI 8610 gas chromatograph using a MXT-1 Restek column. HPLC analyses were performed on a Jasco MD-1515 system equipped with a multiwavelength detector and a Spherisorb ODS-2 column.

Preparation of [VO(O$_2$)HSalhyhb(H$_2$O)]·H$_2$O (1·H$_2$O): KVO_3 (0.69 g, 5 mmol) was dissolved in water (20 mL) and H_2O_2 (0.75 mL of a 30% aqueous solution). A solution of H_2Salhyhb (1.11 g, 5 mmol) in methanol (25 mL) was added dropwise to the KVO_3 solution, which had been cooled to 0 °C, while constantly stirring. The pH of the resulting orange-red solution was adjusted to about 2 with perchloric acid. The solution was stirred at 0 °C for an additional 30 min, and during this time an orange solid precipitated. This was filtered off and washed with cold methanol. The filtrate solution was kept at 5 °C in a closed vessel for about one week. Orange crystals grew, and these were filtered off and dried in vacuo. Yield: 1.38 g (3.9 mmol, 77%). $C_{11}H_{17}N_2O_8V$ (**1**·H_2O) (356.21): calcd. C 37.09, H 4.81, N 7.86; found C 37.73, H 4.71, N 8.09. ^{1}H NMR (400 MHz, CD_3OD): δ = 1.96 (tt, J = 6.8 Hz, 2 H, CH_2CH$_2$OH), 2.52 (t, J = 7.6 Hz, 2 H, CH_2CO), 3.67 (t, J = 6.4 Hz, 2 H, CH_2OH), 4.83 (s, H_2O), 6.91–7.01 (m, 2 H, arom. CH), 7.49–7.58 (m, 2 H, arom. CH), 8.56 (s, 1 H, CH=N) ppm. $^{13}C\{^{1}H\}$ NMR (50 MHz, CD_3OD): δ = 29.0 (*C*H$_2$CO), 30.5 (*C*H$_2$CH$_2$OH), 62.4 (*C*H$_2$OH), 117.7, 121.4, 121.5, 133.4, 133.7 (arom. CH), 153.2 (CH=N), 165.1 (arom. C), 179.7 (C=O) ppm. ^{51}V NMR (105 MHz, CD_3OD): δ = –551 ppm ($\Delta\nu_{1/2}$ = 105 Hz). Selected IR data (KBr): $\tilde{\nu}$ = 978 (V=O), 921 (O–O, peroxo), 765 [asym. V(O)$_2$], 562 [sym. V(O)$_2$] cm^{-1}. ESI-MS (negative mode): m/z = 318.9 [M$^-$, – H, – H_2O].

Bromide Oxidation: The oxidative bromination of 1,3,5-trimethoxybenzene (TMB; 25 mg, 0.15 mmol) with complex **1** (54 mg, 0.15 mmol) in the presence of a 10-fold excess of tetrabutylammonium bromide (0.483 g, 1.5 mmol) and one equivalent perchloric acid, was performed in DMF (30 mL, 5 M in TMB). The reaction (i.e. the formation of Br-TMB) was monitored by HPLC with a Sperisorb ODS-2 column; the solvent system used was a H_2O/CH_3OH (50:50) mixture.

Reaction with Methylphenylsulfane: A solution of complex **1** (19 mg, 0.05 mmol) in a dichloromethane/methanol solution (10 mL of a 7:3 solution) reacted with one equivalent of methylphenylsulfane at room temperature. The reaction (i.e. the formation of methylphenylsulfane oxide) was monitored qualitatively by thin-layer chromatography using an eluent mixture of ethyl acetate/chloroform/methanol (5:10:3), and monitored quantitatively by gas chromatography.

Reaction with Triphenylphosphane: Triphenylphosphane (13 mg, 0.05 mmol) was added to a solution of **1** (19 mg, 0.05 mmol) in acetonitrile (15 mL), and the resulting solution was refluxed for 1 h. Upon cooling to room temperature, a yellow precipitate was formed. This was removed by filtration, and the filtrate solution kept at 5 °C. Additional precipitate formed, which resulted in an overall yield of 9.8 mg (0.03 mmol; 64%) of the *cis*-dioxovanadium(V) complex. ^{51}V NMR (105 MHz, [D$_6$]DMSO): δ = –539 ppm. The formation of triphenylphosphane oxide was monitored by ^{31}P NMR spectroscopy.

X-ray Crystallographic Study for 1·H$_2$O: $C_{11}H_{17}N_2O_8V$, M_r = 356.21 g mol^{-1}, monoclinic, space group $P2_1/n$, a = 1034.3(2), b = 698.86(14), c = 2006.6(4) pm, β = 100.74(3), V = 1425.0(5)·10^6 pm^3, Z = 4, μ(Mo-$K\alpha$) = 0.740 mm^{-1}, 14918 reflections measured with a STOE IPDS imaging plate system at 293 K in the 3.09–29.39° θ range, 3887 unique reflections (R_{int} = 0.1472) were used in the data analysis. The structure was solved by direct methods with SHELXS-97 and subsequently refined against F^2 with SHELXL-97.[27] The refinement converged at $R1$ = 0.0454 for 1467 observed reflections with $I > 2\sigma(I)$, and $wR2$ = 0.0807 for all unique reflections. The goodness-of-fit on F^2 was 0.768. The anisotropic displacement parameters for all non-hydrogen atoms were refined. All hydrogen atoms bonded to carbon atoms were introduced at theoretical positions, and were not refined. The hydrogen atoms bonded to nitrogen and oxygen atoms were located in the difference Fourier map and their isotropic displacement parameters were refined, with the exception of the hydrogen atoms of the free water molecule. The isotropic displacement parameters for these hydrogen atoms were fixed to 1.5 times that of the oxygen atom O8. The largest positive and negative residual Fourier peaks after the refinement were equal to 0.29 and –0.44, respectively. CCDC-258615 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

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